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# EUROPEAN PATENT APPLICATION

21 Application number: 88870068.9

51 Int. Cl.<sup>4</sup>: A 01 N 25/30  
A 01 N 25/02

22 Date of filing: 26.04.88

30 Priority: 29.04.87 GB 8710164  
04.09.87 GB 8720819

43 Date of publication of application:  
09.11.88 Bulletin 88/45

84 Designated Contracting States:  
AT BE CH DE ES FR GB GR IT LI LU NL SE

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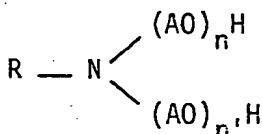
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54 Improved glyphosate formulations.

57 Concentrates containing glyphosate herbicide which on dilution give spray solutions having higher herbicidal unit activity than prior art solutions comprise:

- (a) solubilised glyphosate equivalent to at least 40 grams per litre of glyphosate acid; and
- (b) a surfactant which is (i) an amine having the formula



where R represents a straight- or branched-chain alkyl or alkenyl group having from about 8 to about 22 carbon atoms, A represents an alkylene group, for example an ethylene or propylene group, and n and n' are integers such that n + n' has a value of from 1 to about 12, (ii) a mixture of such amines having different groups R, the average number of carbon atoms in the groups R being from about 8 to about 22, or (iii) a mixture of such amines

having different values of n and n', n and n' being integers such that in individual amines n + n' can have a value from 0 to about 15, but in the mixture the average of the sum of n + n' is from 1 to about 12, R having a single value or an average value as in a mixture (ii); and wherein the weight ratio of (a) (expressed as glyphosate acid equivalent) to (b) is from about 1:1.75 to about 6:1.

EP 0 290 416 A2

## Description

## IMPROVED GLYPHOSATE FORMULATIONS

This invention relates to improved glyphosate formulations.

Glyphosate (N-phosphonomethylglycine) is well known as a foliage-acting herbicide. In the free acid form, glyphosate has low water-solubility, and because of this, commercial formulations contain a water-soluble salt of glyphosate. For example, in Roundup® herbicide, glyphosate is present as the monoisopropylamine salt.

Several studies on the effect of surfactants on the herbicidal activity of the monoisopropylamine salt of glyphosate are reported in the literature. For example, Turner and Loader, Weed Research, 1980, Vol 20, 139-146 reported that fatty amine ethoxylates having a hydrophile-lipophile balance of 17, are generally the most effective in increasing the herbicidal activity of solutions of Roundup® herbicide. In the same publication, the authors state that with spray solutions containing ammonium sulphate, responses to surfactants were different, with lipophilic surfactants, for example fatty amine ethoxylates having a hydrophile-lipophile balance of 6, usually having greater effects.

In 1985 BCPC Monogram No. 28 Symposium on Application and Biology "Studies with Alternative Glyphosate Formulations", Turner and Tabbush describe the results of some trials with glyphosate acid formulated as a foliage spray. In summarising the results, they state that glyphosate acid had relatively little activity unless surfactants and/or ammonium sulphate was added, but that when this was done, its phytotoxicity was equivalent to that of Roundup® herbicide. There is an observation that glyphosate acid is much more soluble in a solution of a tertiary amine from tallow containing 15 mols of ethylene oxide per mol of amine than in pure water.

US-A-4 612 034 describes herbicidal formulations comprising mixtures of the isopropylamine salt of glyphosate and a potentiating amount of a specified class of thiocyanates including ammonium thiocyanate.

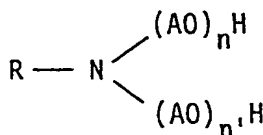
In the experiments described in 1985 BCPC Monogram No. 28 on the preparation of salts of glyphosate or the solubilisation of glyphosate acid with ethoxylated fatty acid amines, the ethoxylated fatty acid amine surfactant was used in an excess of at least five parts by weight per part by weight of glyphosate acid. While one experiment described in Weed Research, 1980, Vol 20, 139-146, uses a solution containing less surfactant than glyphosate (as Roundup® herbicide, which itself contains a significant amount of surfactant) it was applied by a controlled drop technique at 20 l/ha. For experiments in which solutions were sprayed by conventional techniques at normal farm application rates of about 200 l/ha, however, the solutions contained about twice as much surfactant as glyphosate.

In the investigations leading to the present invention, we worked at conventional spray rates, and with solutions containing lower surfactant to glyphosate ratios than those disclosed in the prior art for solutions sprayed at those rates. We have found that with our solutions, better results are obtained under most conditions with the lipophilic fatty amine ethoxylates than with the more hydrophilic fatty amine ethoxylates hitherto thought to be optimum. This is so, whether or not the solution also contains ammonium sulphate. These observations are surprising in view of the prior art which suggests that the lipophilic surfactants would not be the surfactants of choice except in the presence of ammonium sulphate.

The present invention provides commercially attractive glyphosate compositions particularly adapted for use in conjunction with agriculturally-acceptable inorganic ammonium salts such as ammonium sulphate for spraying at conventional volume rates. A feature of the present invention is that the amount of alkoxylated amine surfactant relative to total glyphosate can be reduced significantly below the ratio disclosed in the prior art for conventional spray solutions, while maintaining the herbicidal activity per unit of glyphosate. Alternatively, the unit activity can be enhanced at a ratio of surfactant to glyphosate similar to that of the prior art.

In one aspect, a composition of the invention is a concentrate comprising an aqueous solution containing

- (a) solubilised glyphosate equivalent to at least 40 grams per litre of glyphosate acid; and
- (b) a surfactant which is (i) an amine having the formula



where R represents a straight- or branched-chain alkyl or alkenyl group having from about 8 to about 22 carbon atoms, A represents an alkylene group, for example an ethylene or propylene group, and n and n' are integers such that n + n' has a value of from 1 to about 12, (ii) a mixture of such amines having different groups R, the average number of carbon atoms in the groups R being from about 8 to about 22, or (iii) a mixture of such amines having different values of n and n', n and n' being integers such that in individual amines n + n' can have a value from 0 to about 15, but in the mixture the average of the sum of n + n' is from 1 to about 12, R having a single value or an average value as in a mixture (ii); and wherein the

weight ratio of (a) (expressed as glyphosate acid equivalent) to (b) is from about 1:1.75 to about 6:1.

A further aspect of the invention is a spray solution intended for spraying at conventional volume rates and containing solubilised glyphosate and surfactant as defined above in a weight ratio of glyphosate (expressed as glyphosate acid equivalent) to surfactant of from about 1:1.75 to about 6:1. A herbicidal method comprises spraying weeds with the said spray solution at 100-400 litres per hectare, the concentration of (a) in the spray solution being such that the application rate of glyphosate acid equivalent is from 0.125 to 1.5 kg per hectare.

In the compositions of the invention, the glyphosate is solubilised by the presence in the solution of one or more agriculturally-acceptable cations. Such cations include the cationic forms of the alkoxyated amine surfactants, alkali metal cations, for instance sodium and potassium, and ammonium and substituted ammonium cations. The latter include cations derived from primary or secondary amines such as isopropylamine or dimethylamine and from diamines such as ethylenediamine. Other examples of agriculturally acceptable salts of glyphosate are aminoguanidine salts and trialkylsulphonium salts, for example the trimethylsulphonium salt, as disclosed respectively in EP-A-O 088 180 and US-A-4 405 531.

Formulations containing (a) and (b) in ratios towards the lower (1:1.75) end of the range stated above can be prepared from low molecular weight surfactants by the solubilisation of glyphosate acid with the surfactant alone. In most embodiments however, the upper limitation on the amount of surfactant requires the solution to contain other agriculturally acceptable cations in addition to the surfactant cations. In these embodiments, the solubilised glyphosate can be derived (i) partly from glyphosate acid solubilised by means of the surfactant and partly from a salt of glyphosate with another agriculturally-acceptable cation, or (ii) wholly from a salt of glyphosate with such another agriculturally-acceptable cation.

As discussed later, the concentrates of the invention may contain a significant amount of an agriculturally acceptable inorganic ammonium salt in addition to components (a) and (b). Concentrates containing no significant amount of such salt may contain up to 450 g/l, for example from 150-450 g/l or even more, of glyphosate acid equivalent at ambient temperatures, depending on the water-solubility of the glyphosate salt. For example, when the glyphosate salt is the monoisopropylamine salt, solutions containing 250-400 g/l of glyphosate acid equivalent are easily prepared. Mono-ammonium glyphosate shows similar solubility characteristics but certain alkali metal salts, for example the potassium salt are somewhat less soluble. In such cases, the maximum concentration of soluble glyphosate obtainable, expressed as glyphosate acid equivalent, is perhaps 250-300 g/l.

In general, on economic grounds, concentrates of the invention containing a minimum of water, i.e. solutions that are substantially saturated, are preferred. Depending on the climatic conditions to which the solutions are likely to be subjected between manufacture and use, they can be made so that they are saturated at, for example, -5°C, 0°C or +10°C. Normally a safety margin will be provided, so that a solution which would not be expected to experience temperatures below 10°C, for instance, would nevertheless be stable (i.e. not deposit solids) at, for instance, 5°C. In addition, the concentrates of the invention can contain conventional anti-freeze additives such as ethylene glycol, polyethylene glycols or glycerol.

In the compositions of the invention, the weight ratio of total glyphosate (expressed as glyphosate acid equivalent) to surfactant is from about 1:1.75 to about 6:1. The maximum amount of surfactant is determined mainly by economic considerations. Higher levels of surfactant may increase the unit herbicidal effect of the glyphosate, but these are not cost-effective beyond a certain level. When the concentrates are viewed as precursors of spray solutions which also contain an agriculturally acceptable inorganic ammonium salt, there is little advantage in using more surfactant than 1.5 parts per part by weight of glyphosate acid equivalent. At the other end of the range, the maximum preferred glyphosate : surfactant weight ratio is about 4:1. More preferred ranges of ratios are from 1:1 to 3:1, for example from 1.5:1 to 2.5:1, although the limits can vary depending on the particular surfactant used.

Commercially available amine surfactants within the above formula are often mixtures rather than single compounds. They include alkoxyated derivatives of "cocoamine" in which the groups R correspond to alkyl groups derived from myristic, lauric, palmitic and stearic acids. The average number of carbon atoms in R in cocoamine is 12-14. Other examples are alkoxyated derivatives of "oleylamine", where the principal carbon chain of R corresponds to that of oleic acid (18 carbon atoms), with small amounts of shorter and longer chains, of stearylamine (18 carbon atoms), and of "tallow amine". In tallow amine, R is mainly a mixture of hexa-decyl and octadecyl. The commercial surfactants are also usually mixtures of molecules having various values of  $n + n'$ , and surfactants having a low average value of  $n + n'$  may contain a proportion of non-alkoxyated or mono-alkoxyated amines. The preferred alkoxyated derivatives are the ethoxyated derivatives.

In general, lower molecular weight surfactants are preferred to higher molecular weight surfactants, because a given weight of the former provides a higher molecular concentration of surfactant than the same weight of the latter. The most preferred surfactants are those where A represents an ethylene group, and those where the number or average number of carbon atoms in the group or groups R is from about 10 to about 20. As regards the value or average value of  $n + n'$ , in preferred surfactants this lies in the range from about 1.5 to about 12, more especially in the range from about 2 to about 10. Specific examples of preferred surfactants are ethoxyated derivatives of cocoamine, tallow amine and oleylamine where in each case  $n + n'$  has an average value of about 2, about 5 or about 8.

For the preparation of concentrates of the invention where the cationic form of the surfactant is at least partially responsible for the solubility of the glyphosate, a solution of solubilised glyphosate acid can in many

instances be made simply by mixing the acid and the alkoxylated amine surfactant in an aqueous medium at room temperature or slightly above. A clear solution is obtained within a few minutes. The amount of surfactant required to solubilise the glyphosate acid is normally about 1:1 molar equivalent amount. However, slightly less, for example 90% of the molar equivalent amount, may be sufficient in certain instances, while in others it may be preferable to use a small excess, for instance up to 30% molar excess of the surfactant. Considerations determining the maximum amount of surfactant employed are discussed above. Where it is necessary to provide part of the glyphosate in the form of a salt of glyphosate with another agriculturally-acceptable cation, the solubilised glyphosate acid solution is then mixed with a solution of the glyphosate salt in the proportions to provide the required amounts of each component in the final concentrate. Concentrates of the invention where a cation other than the cationic form of the surfactant is present in sufficient amount alone to solubilise the glyphosate can be prepared by simply mixing the components at room temperature. The surfactants are normally viscous materials which slowly dissolve when stirred with an aqueous solution of the glyphosate salt. Also, if required, a solution of an agriculturally-acceptable ammonium salt can be incorporated at this stage. In general, the solutions employed throughout will be relatively concentrated or even substantially saturated, to minimise the amount of water in the concentrate. If necessary, however, some adjustment in this respect can be made after mixing, by evaporation or addition of water.

Examples of agriculturally acceptable inorganic ammonium salts known to be effective in enhancing the herbicidal effect of glyphosate and other water-soluble or water-solubilisable herbicides include ammonium sulphate, ammonium nitrate, ammonium phosphate, ammonium sulphamate and ammonium thiocyanate. Of these ammonium sulphate is generally preferred.

In concentrates that contain ammonium salt, the amount so included will depend on its solubility in the presence of the other components. To achieve a given level of ammonium salt, however, adjustments in the amounts of the other components can be made. Generally, the amount will be at least 0.5 parts, for example from 1 to 10 parts, by weight of ammonium salt per part by weight of component (a). These concentrates typically contain at least 70 g/l, for example from 80 to 150 g/l of component (a) and from 100 to 500 g/l of ammonium salt, and the weight ratio of component (a) (expressed as glyphosate acid equivalent) to component (b) is typically from about 1:1 to about 1:1.75.

An example of a specific composition is as follows:

Glyphosate acid	74 g/l
Glyphosate monoisopropylamine salt (expressed as acid equivalent)	49 g/l
C 2 <sup>1</sup> surfactant	120 g/l
Ammonium sulphate	280 g/l

A preferred class of concentrates containing an ammonium salt are compositions which contain 80 to 130 grams per litre of component (a), present as the salt of glyphosate with monoisopropylamine, and 100 to 180 grams per litre of component (b), component (b) being an ethoxylated cocoamine derivative with  $n + n'$  having an average value of about 2, and from 260 to 320 grams per litre of ammonium sulphate.

The present invention includes a herbicidal spray solution for spraying at conventional volume rates, and which contains

(a) a solubilised glyphosate component, said glyphosate being present (i) partly as glyphosate acid solubilised by means of a surfactant as defined above and partly as a salt of glyphosate with another agriculturally-acceptable cation, (ii) wholly as glyphosate acid solubilised by means of a said surfactant, or (iii) wholly as a salt of glyphosate with an agriculturally-acceptable cation other than the cationic form of the surfactant, and

(b) a surfactant as defined above, the weight ratio of (a) (expressed as glyphosate acid equivalent) to (b) being from about 1:1.75 to about 6:1.

The concentration of glyphosate in the spray solution will typically be such that when sprayed at 100-400 litres per hectare, the application rate of glyphosate acid equivalent is from 0.125 to 1.5 kg per hectare.

Preferably such a spray solution also contains a water-soluble, agriculturally-acceptable inorganic ammonium salt. The amount of the inorganic ammonium salt used can vary according to the weeds to be treated, the available spray equipment, climatic conditions, etc. Typically, however, the solution will be sprayed at 100-600 l/ha, for example at 100-400 l/ha, and at a dosage rate of at least 0.125 kg/ha glyphosate acid equivalent, and the solution will contain at least the same weight concentration of ammonium salt as glyphosate acid equivalent. For example, the weight ratio of glyphosate acid : ammonium salt in the solution can range from 1:1 to 1:10. The effect of the ammonium salt in enhancing the herbicidal activity of the glyphosate increases rapidly as this ratio is increased at the lower end of the range but less rapidly beyond the mid-point. With ammonium sulphate, the optimum ratio is often from about 1:2 to about 1:7. Dosage rates within the range 0.25-1.5 kg/ha glyphosate acid equivalent, using solutions containing from 5 to 100 g/l, especially from 5 to 30 g/l, of inorganic ammonium salt, are very effective.

A preferred method for preparing a herbicidal spray solution as described above is to mix a concentrate of the invention with water and preferably with an ammonium salt, but if desired, the individual components of the solution can be mixed in a spray tank with the required volume of water.

The concentrates and solutions of the invention may contain optional additional components. As indicated

<sup>1</sup> An ethoxylated derivative of cocoamine containing an average of about 2 ethoxy groups.

above, these include anti-freeze agents. Other examples are dyes, thickening agents, anti-foam agents, for instance silicone-based anti-foam agents, and secondary surfactants, for instance non-ionic surfactants such as polyoxyethylene ethers or esters. The concentrates and solutions of the invention may also be mixed with other water-soluble herbicides, for example but not limited to, salts of 2,4-dichlorophenoxyacetic acid or of 4-chloro-2-methylphenoxyacetic acid, or with finely-divided water-soluble herbicides, for example but not limited to, triazines or substituted ureas.

The invention is illustrated by the following examples.

Tables 1 to 3 show solutions of the invention where solubilisation of glyphosate acid relies at least in part on the presence of the cationic form of the surfactant. These solutions were prepared by first solubilising glyphosate acid (crystals containing 9% by weight of water) by stirring in water at room temperature or at a temperature not exceeding 60°C, with about 1.05 molar equivalents of ethoxylated amine surfactant per mole of glyphosate acid. When required, the solution thus obtained was then mixed with a solution of a mono salt (ammonium, isopropylamine or potassium) of glyphosate and, if required, water, to give solutions having concentrations and ratios of glyphosate acid equivalent: surfactant shown in the Tables below.

In the Tables, which show the percentages by weight of the various components, the surfactants are identified by the initial letter of the amine and by the average number of ethoxide groups. Thus C 2 indicates a surfactant derived from cocoamine and having an average of 2 ethoxide groups; O 5 indicates a surfactant derived from oleylamine and having an average of 5 ethoxide groups; S 8 indicates a surfactant derived from stearylamine and having an average of 8 ethoxide groups; and T 10 indicates a surfactant derived from tallowamine and having an average of 10 ethoxide groups, etc. Glyphosate salts are identified as AM (ammonium), IP (isopropylammonium) or K (potassium).

The solutions of Table 1 contained approximately 300 g/l of glyphosate acid equivalent and 150 g/l of surfactant. The latter corresponds to 13.64% by weight of surfactant in the solution. The glyphosate salt was the monoisopropylamine salt.

Table 1

Solution No.	91% glyphosate acid (%)	Surfactant	Glyphosate salt (%)
1	8.92	C2	41.69
2	6.09	C5	47.30
3	4.62	C8	50.20
4	7.22	O2	45.06
5	5.25	O5	48.97
6	4.12	O8	51.20
7	4.15	S8	51.14
8	5.30	T5	48.86
9	4.15	T8	51.14
10	3.63	T10	52.17
11	2.76	T15	53.90

Table 2 gives the percent by weight of components in a series of solutions containing glyphosate acid, the monoisopropylamine salt of glyphosate and an ethoxylated surfactant, and in which the solutions have different weight ratios of glyphosate acid equivalent (a.e.) to surfactant.

Table 2

	Solution No.	91% Glyph acid (%)	Glyph salt (%)	Surfactant (%)	Code	Glyph a.e.to surfactant ratio	Glyph a.e. g/l
5							
10	12	8.92	12.02	13.64	C2	1:1	145
	13	5.10	57.74	7.80	C2	4:1	360
15	14	4.85	21.51	14.29	C8	1:1	154
	15	2.77	65.75	8.18	C8	4:1	383
	16	7.67	15.91	14.29	T2	1:1	151
20	17	7.32	44.86	13.64	T2	2:1	300
	18	4.39	62.55	8.18	T2	4:1	379

Table 3 gives the percent by weight of components in solutions where the glyphosate salt is the ammonium (AM) or potassium (K) salt. In all solutions the weight ratio of glyphosate acid equivalent to surfactant is 2:1.

Table 3

	Solution No.	91% Glyphosate acid (%)	Glyphosate salt (%)	Code	Surfactant (%)	Code
35						
40	19	8.92	67.04	K	13.64	C2
	20	8.92	60.23	AM	13.64	C2
	21	3.73	77.25	K	12.73	C10
45	22	3.98	74.36	AM	13.64	C10
	23	7.32	72.13	K	13.64	T2
	24	7.32	64.81	AM	13.64	T2
50	25	3.39	78.30	K	12.73	T10
	26	3.63	75.37	AM	13.64	T10

Solutions 21 and 25 contained approximately 280 g/l and 140 g/l of glyphosate acid equivalent and surfactant respectively. In the other solutions, the corresponding figures are 300 g/l and 150 g/l.

Table 4 shows compositions of the invention which were prepared by stirring a 62% by weight aqueous solution of the mono-isopropylamine salt of glyphosate at room temperature with the required amount of surfactant, and, then, if required, with a saturated solution of ammonium sulphate.

Table 4

Solution No.	Surfactant Code - g/l	Glyphosate (Acid Equivalent) g/l	Ammonium Sulphate g/l	Weight Ratio Glyphosate a.e. to surfactant	
27	C 2 - 180	360	-	2 : 1	10
28	C 2 - 200	400	-	2 : 1	
29	C 2 - 120	120	280	1 : 1	15
30	C 2 - 140	90	300	1 : 1.56	
31	C 5 - 202	404	-	2 : 1	
32	C 10 - 204	407	-	2 : 1	20
33	O 8 - 203	405	-	2 : 1	
34	S 10 - 203	406	-	2 : 1	
35	T 5 - 201	402	-	2 : 1	25
36	C 2 - 220	120	-	1 : 1.75	
37	C 2 - 150	150	-	1 : 1	
38	C 2 - 100	399	-	4 : 1	30
39	C 2 - 59	356	-	6 : 1	

In the drawings, Fig 1 shows results obtained in growth room tests on wheat, Figs 2, 3, 4, 10 and 11 show results obtained in growth room tests on blackgrass (*Alopecurus myosuroides*), and Figs 5 and 6 show results obtained in a field trial on wheat stubble. As volunteer wheat, wheat is a weed in its own right. Also, its response to glyphosate is typical of that of a range of weed grasses. Figs 7 and 8 show results obtained in a field trial in sown pasture containing perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*), and Fig 9 shows results obtained on the perennial grass weed couch (*Elymus repens*) in cereal stubble.

Growth room herbicidal evaluations were carried out using the following procedure. Plants were grown from seed in 13 cm pots containing a natural sandy loam soil. All irrigation was supplied automatically from below, mineral nutrients being added to the irrigation supply as required. The pots were placed in Conviron growth rooms with a 14 hour photoperiod, illuminance of 600 microeinsteins m<sup>-2</sup>s<sup>-1</sup> and a temperature regime of 15°C (day), 9°C (night). About two weeks before spraying, (2-4 weeks after sowing) plants were thinned by hand to leave a uniform stand.

At least one week before treatment, the plants were moved to a larger growth room with precise relative humidity as well as temperature control; the RH regime employed was 50% (day), and 65% or 75% (night). Plants remained in this room for the remainder of the experiment. Before spraying, pots were selected for uniformity as far as possible and atypical examples were discarded. Spray solutions were applied with a Mardrive precision laboratory sprayer, calibrated to deliver 200 l/ha spray solution in a single pass. All replicate pots (3-5 per species per treatment) were sprayed with one pass of the sprayer.

After treatment, untreated control pots were placed at random among treated pots. Assessment of "% Phytotoxicity" was made by comparison with untreated controls on an arbitrary scale from 0 to 100%, where 0 means no visible effect and 100% means complete death. For any one assessment, all pots were rated by the same individual, assessments being performed "blind", without knowledge of the treatment. The blocks in Figs 2, 3, 4, 10 and 11 show the averages of observations on the 3-5 replicates used.

The trial which gave the results shown in Figs 5 and 6 was carried out in a field of wheat stubble which was 75% covered by weeds. About 35% of the weeds were volunteer wheat, and the remainder were a mixture of annual broadleaves, 35% chickweed (*Stellaria media*), 10% field pansy (*Viola arvensis*) and 10% Scarlet Pimpernel (*Anagallis arvensis*). The air temperature was 23°C, soil temperature 15°C, relative humidity 48%, with zero wind velocity. The test design was a randomised complete block with four replicates and a unit pl<sup>1</sup> siz<sup>1</sup> of 18m<sup>1</sup>. The observations recorded are % foliage kill three weeks after treatment.

The trial which gave the results shown in Figs 7 and 8 was carried out in sown pasture containing in one part a pure stand of perennial ryegrass and in another part a mixture of various grasses and white clover. Data are shown for perennial ryegrass and white clover only. During spraying the air temperature was 18°C and there

was a slight to moderate wind. No rain fell for 2 days after spraying. The test design was a randomised complete block with three replicates of each treatment and twelve replicates of untreated plots. Plot size was 16m<sup>2</sup> in the perennial ryegrass sward plus 16m<sup>2</sup> in the mixed grass and clover sward. The observations recorded are % foliage kill 47 days after treatment.

The trial which gave the results shown in Fig 9 was conducted in a field of cereal stubble carrying a moderate infestation of couch, fairly uniformly distributed over the trial area. During spraying the air temperature was 15°C and there was a light to moderate wind. No rain fell for 5 days after spraying. The test design was a randomised complete block with three replicates and a plot size of 30m<sup>2</sup>. The observations recorded are % foliage kill 25 days after treatment.

In preparing spray solutions, concentrates described in the Table above were diluted with water so that at a spray volume equivalent to 200 l/ha, application rates in kg glyphosate acid equivalent/ha were as indicated in Figs. 1-11.

The spray solutions containing ammonium sulphate in the tests of Fig 1 contained 6 parts by weight of ammonium sulphate per part by weight of glyphosate acid equivalent. The spray solutions containing ammonium sulphate used in the tests of Figs 2, 3 and 4 and in the field trial of Figs 5 and 6 contained 10 g/l of ammonium sulphate. The spray solutions containing ammonium sulphate in the field trials of Figs. 7, 8 and 9 contained 3.6 parts by weight of ammonium sulphate per part by weight of glyphosate acid equivalent.

The spray solutions used for comparative purposes (Controls) contained glyphosate wholly as the monoisopropylamine salt, and an ethoxylated tallow amine-based surfactant having an average of 15 ethoxide units. In Control 1, the weight ratio was 2.94 parts of surfactant to 1 part of glyphosate acid equivalent; in Control 2 it was 2 parts of surfactant to 1 part of glyphosate acid equivalent, and in Control 3 the weight ratio was 1 part of surfactant to 2 parts of glyphosate acid equivalent. These ratios are similar to those in existing commercial formulations of glyphosate.

In the Figures, spray solutions are designated as "Formulations" and numbered according to the number of the concentrate in the Tables above from which they are derived.

Fig 1 shows that on wheat, at all rates of application, herbicidal activity is at least as high for Formulation No. 1 of the invention with a 2:1 glyphosate a.e.:surfactant weight ratio and ammonium sulphate as for Control 1, despite the presence in this Control of almost 6 times as much surfactant per unit of glyphosate a.e. as in the formulation of the invention. When compared with Control 3, which has the same glyphosate : surfactant ratio as Formulation No. 1 of the invention, Formulation No. 1 with no ammonium sulphate was as active at 0.18, 0.36 and 0.72 kg a.e./ha as Control 3 at twice these dosage rates, namely 0.36, 0.72 and 1.44 kg a.e./ha respectively. With the addition to Formulation No. 1 of ammonium sulphate, it became almost as active at 0.09, 0.18 and 0.36 kg a.e./ha as Control 3 at four times these dosage rates.

Fig 2 shows the results obtained 14 days after treatment with spray solutions containing C 2 as the surfactant on blackgrass. Decrease in activity occurs as the proportion of surfactant is decreased, but the rate of the decrease is substantially less for solutions containing ammonium sulphate. Formulation 1 with ammonium sulphate (ratio of glyphosate acid equivalent : surfactant of 2:1) has better activity at the lower dosage rates, and substantially the same activity at the top rate as Control 2, despite the lower levels of surfactant. Formulation 12 with ammonium sulphate (ratio of glyphosate acid equivalent : surfactant of 1:1) had better activity at all levels than Control 2. At 0.5 kg glyphosate a.e./ha, Formulation 13 with ammonium sulphate had practically the same phytotoxicity as Control 2 and greater phytotoxicity than Control 3, despite the significantly lower level of surfactant relative to glyphosate.

Fig 3 shows the results obtained 14 days after treatment with spray solutions containing C 8 as the surfactant on blackgrass. A more pronounced decrease in activity occurs as the proportion of surfactant is decreased than with surfactant C 2. Nevertheless, Formulation 14 containing ammonium sulphate and having a ratio of glyphosate acid equivalent : surfactant of 1:1 has substantially the same activity at all dosage rates as Control 2 which has twice the level of surfactant. At the lowest rate of application, Formulation 3 is significantly more active than Control 3 with the same surfactant to glyphosate ratio.

Fig 4 shows results obtained 14 days after treatment with formulations containing monoisopropylamine glyphosate (1 and 10), ammonium glyphosate (20 and 26) and potassium glyphosate (19 and 25). All the formulations have a glyphosate acid equivalent to surfactant weight ratio of 2:1, the same as Control 3. The generally enhanced herbicidal activity of the formulations relative to this control is clear, and in some instances the formulations with ammonium sulphate have phytotoxicities at least as high as Control 2 which has four times the level of surfactant.

Fig 5 shows that on volunteer wheat at 0.27 kg a.e./ha, the performance of Formulation No. 1 is enhanced by the addition of ammonium sulphate to a level at which the performance is substantially the same as that of Control 1, despite a much lower surfactant : glyphosate acid equivalent ratio. At 0.54 kg a.e./ha the addition of ammonium sulphate had virtually no effect on the performance of Formulation No. 1. With or without ammonium sulphate, it was substantially the same as the control.

Fig 6 shows the herbicidal effect of glyphosate formulations on annual broadleaves. The formulation of the invention is equivalent to Control 1 at 0.54 kg a.e./ha despite the lower surfactant level.

Figs 7 and 8 show the herbicidal effect of Formulation No. 1 on perennial ryegrass and white clover. On both species the formulation of the invention was equal or superior in activity to Control 1, despite its much lower surfactant level, and showed activity equal or superior to that of Control 3 having the same surfactant level but applied at twice the dosage rate. Addition of ammonium sulphate gave a slight further increase in the activity of



## Formulation No. 1.

Fig 9 shows the herbicidal effect of formulations of the invention on couch. Both Formulation No. 1 and No. 13, with the addition of ammonium sulphate, were more active than Control 1 which contains almost 6 times as much surfactant per unit of glyphosate a.e. as Formulation 1 and almost 12 times as much as Formulation No. 13. Both formulations of the invention at 0.18 and 0.36 kg a.e./ha were equal to Control 3 applied at four times these dosage rates, namely 0.72 and 1.44 kg a.e./ha respectively.

Fig 10 shows results obtained 22 days after treatment with spray solutions prepared by the dilution of concentrates containing various surfactants and glyphosate derived wholly from the isopropylamine salt. In all solutions, glyphosate and surfactant were present in the ratio 2:1. At the lowest rate of application, all solutions of the invention were more active than the control. At 0.25 kg glyphosate acid equivalent/ha, all solutions except those having C 10 or O 8 as the surfactant were more active than the control. With solutions containing ammonium sulphate (not shown), all were more active than the control at 0.125 kg glyphosate acid equivalent/ha, and all except that containing C 10 as the surfactant were more active than the control at 0.25 kg glyphosate acid equivalent/ha.

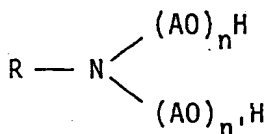
Fig. 11 shows the results obtained 22 days after treatment using a series of spray solutions containing C 2 as the surfactant and with decreasing proportions of surfactant. The glyphosate in these solutions is derived wholly from the monoisopropylamine salt. Decrease in activity occurs as the proportion of surfactant decreases, but at the lowest rate of application the solution of the invention (from concentrate No. 38) containing glyphosate and surfactant in the ratio 4:1 was over twice as active as the control containing twice as much surfactant. At the higher rates of application it was at least as active as the control. A similar pattern was observed with spray solutions containing 1% of ammonium sulphite (not shown). At all rates of application, the solution containing glyphosate and surfactant in the ratio 4:1 was more active than the control containing twice as much surfactant.

## Claims

1. A composition which comprises an aqueous solution containing

(a) solubilised glyphosate in amount equivalent to at least 40 grams per litre of glyphosate acid,

(b) a surfactant which is (i) an amine having the formula



where R represents a straight- or branched-chain alkyl or alkenyl group having from about 8 to about 22 carbon atoms, A represents an alkylene group, and n and n' are integers such that n + n' has a value of from 1 to about 12, (ii) a mixture of such amines having different groups R, the average number of carbon atoms in the groups R being from about 8 to about 22, or (iii) a mixture of such amines having different values of n and n', n and n' being integers such that in individual amines n + n' has a value from 0 to about 15, but in the mixture the average of the sum of n + n' is from 1 to about 12, R having a single value or an average value as in a mixture (ii);

and wherein the weight ratio of (a) (expressed as glyphosate acid equivalent) to (b) is from about 1:1.75 to about 6:1.

2. A composition according to Claim 1 wherein the weight ratio of component (a) to surfactant is from about 1:1 to about 4:1.

3. A composition according to Claim 2 wherein the weight ratio of component (a) to surfactant is from about 1.5:1 to about 3:1.

4. A composition according to any of Claims 1 to 3 in which A in the formula of the surfactant represents an ethylene or propylene group and the surfactant is a mixture in which n + n' has an average value of from about 1.5 to about 12.

5. A composition according to Claim 4 in which A represents an ethylene group.

6. A composition according to Claim 5 wherein the number or average number of carbon atoms in R is from about 8 to about 18, and the average value of n + n' is from about 2 to about 10.

7. A composition according to Claim 6 wherein the surfactant is an ethoxylated derivative of cocoamine, tallow amine or of oleylamine where n + n' has an average value of about 2, about 5 or about 8.

8. A composition according to any of Claims 1 to 7 wherein the glyphosate is present (i) partly as glyphosate acid solubilised by means of the surfactant (b) and partly as a salt of glyphosate with an agriculturally-acceptable cation other than the cationic form of the surfactant, or (ii) wholly as glyphosate acid solubilised by the surfactant.

9. A composition according to Claim 8 wherein the amount of surfactant is at least 90% of the 1:1 molar equivalent of the glyphosate acid.

10. A composition according to either of Claims 8 and 9 wherein the salt of glyphosate is the isopropylamine salt.

11. A composition according to any of Claims 1 to 7 wherein the glyphosate is present wholly as a salt of glyphosate with an agriculturally-acceptable cation other than the cationic form of the surfactant.

12. A composition according to Claim 11 wherein the salt of glyphosate is the isopropylamine salt.

13. A composition according to any of Claims 1 to 12 consisting essentially of an aqueous solution of components (a) and (b) and containing from 150 to 450 grams per litre of component (a).

14. A composition according to Claim 11 consisting essentially of an aqueous solution containing from 340 to 420 grams per litre of component (a) and wherein the salt of glyphosate is the monoisopropylamine salt, the surfactant is an ethoxylated cocoamine derivative with  $n + n'$  having an average value of about 2, and the weight ratio of (a) to (b) is about 2:1.

15. A composition according to any of Claims 1 to 12 which comprises an aqueous solution containing an agriculturally-acceptable inorganic ammonium salt in addition to components (a) and (b).

16. A composition according to Claim 15 which contains from 80 to 150 grams per litre of component (a) and from 100 to 500 grams per litre of ammonium salt.

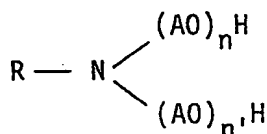
17. A composition according to either of Claims 15 and 16 wherein the ammonium salt is ammonium sulphate.

18. A composition according to Claim 11 which contains 100 to 130 grams per litre of component (a), 100 to 180 grams per litre of component (b), component (a) being the isopropylamine salt of glyphosate and component (b) being an ethoxylated cocoamine derivative with  $n + n'$  having an average value of about 2, and from 260 to 320 grams per litre of ammonium sulphate.

19. A herbicidal method which comprises spraying weeds with a spray solution at 100-400 litres of solution per hectare, said solution containing

(a) solubilised glyphosate, and

(b) a surfactant which is an amine having the formula



where R represents a straight- or branched-chain alkyl or alkenyl group having from about 8 to about 22 carbon atoms, A represents an alkylene group, and  $n$  and  $n'$  are integers such that  $n + n'$  has a value of from 1 to about 12, (ii) a mixture of such amines having different groups R, the average number of carbon atoms in the groups R being from about 8 to about 22, or (iii) a mixture of such amines having different values of  $n$  and  $n'$ ,  $n$  and  $n'$  being integers such that in individual amines  $n + n'$  can have a value from 0 to about 15, but in the mixture the average of the sum of  $n + n'$  is from 1 to about 12, R having a single value or an average value as in a mixture (ii);

the weight ratio of (a) (expressed as glyphosate acid equivalent) to (b) in the spray solution being from about 1:1.75 to about 6:1, and the concentration of (a) in the spray solution being such that the application rate of glyphosate acid equivalent is from 0.125 kg to 1.5 kg per hectare.

20. A method according to Claim 19 in which the spray solution also contains an agriculturally-acceptable inorganic ammonium salt.

21. A method according to Claim 20 wherein the weight ratio of glyphosate, (expressed as glyphosate acid equivalent) to ammonium salt in the solution is from about 1:1 to about 1:10.

22. A method according to either of Claims 20 and 21 wherein the ammonium salt is ammonium sulphate.

23. A method according to Claim 22 wherein the weight ratio of glyphosate (expressed as glyphosate acid equivalent) to ammonium sulphate is from about 1:2 to about 1:7.

24. A method according to Claim 19 in which the spray solution is a solution that has been prepared by mixing a composition according to Claim 14 with water and with an agriculturally-acceptable inorganic ammonium salt.

25. A method according to Claim 19 in which the spray solution is a solution that has been prepared by mixing a composition according to Claim 18 with water.

Fig 1

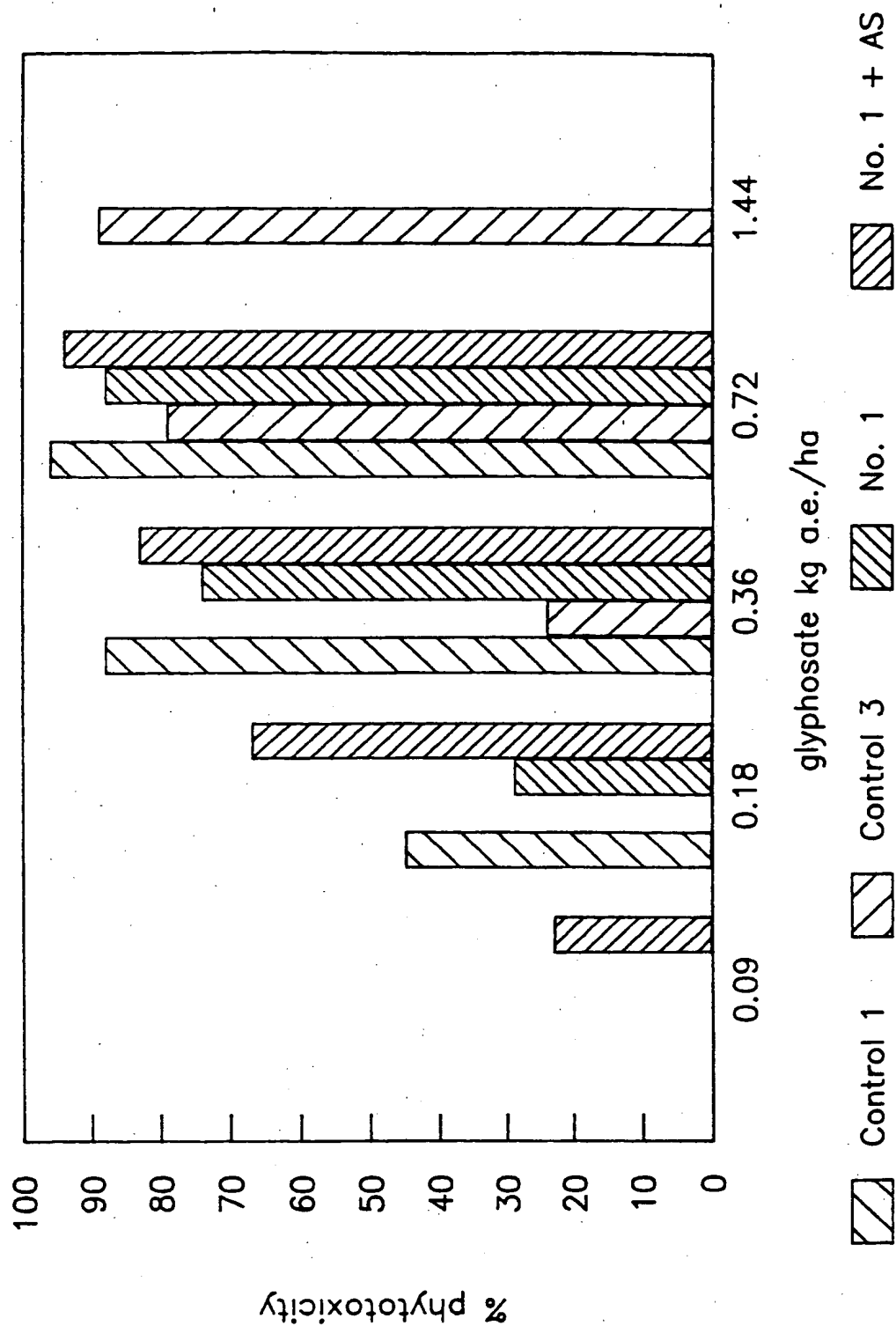


Fig. 2

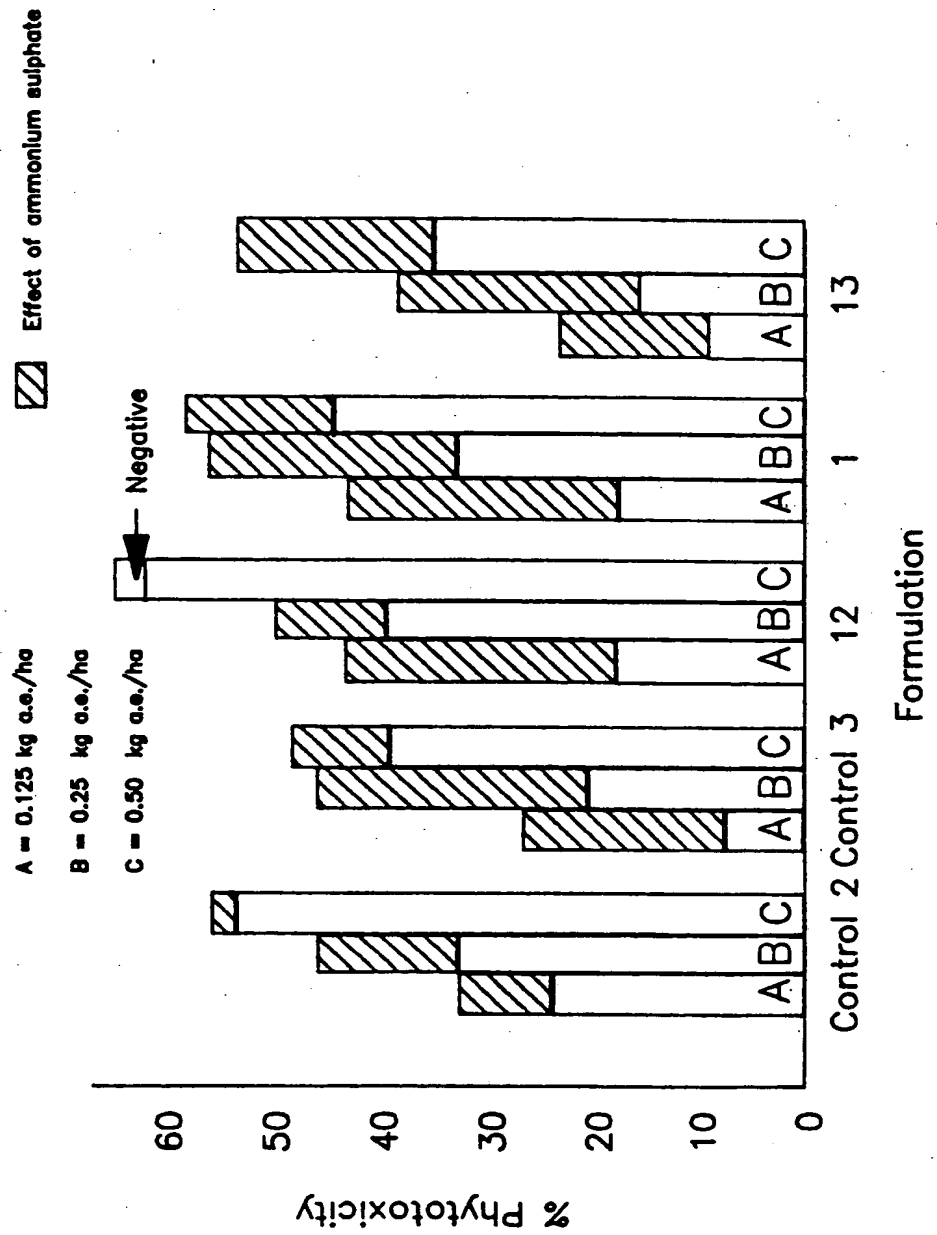



Fig. 3

  $(\text{NH}_4)_2\text{SO}_4 + \text{ve}$

  $(\text{NH}_4)_2\text{SO}_4 - \text{ve}$

A = 0.125 kg a.e./ha

B = 0.25 kg a.e./ha

C = 0.50 kg a.e./ha

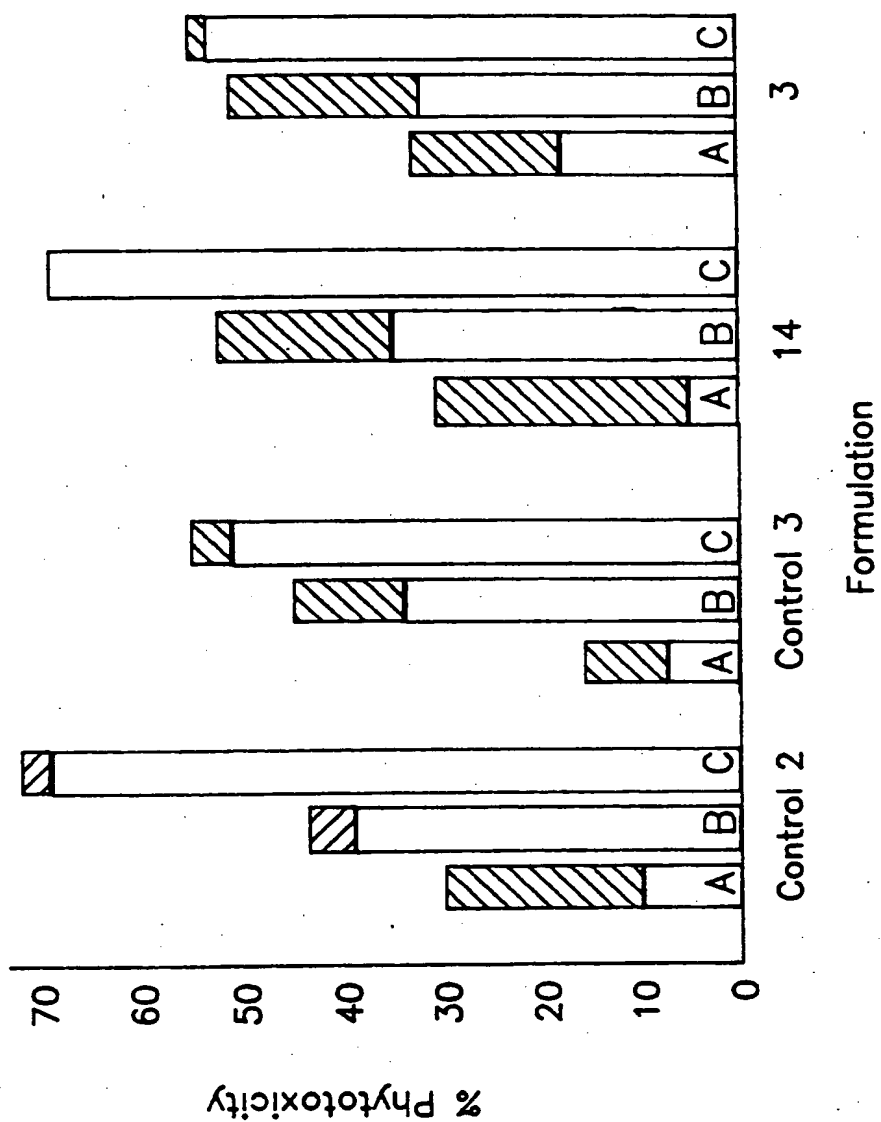


Fig. 4

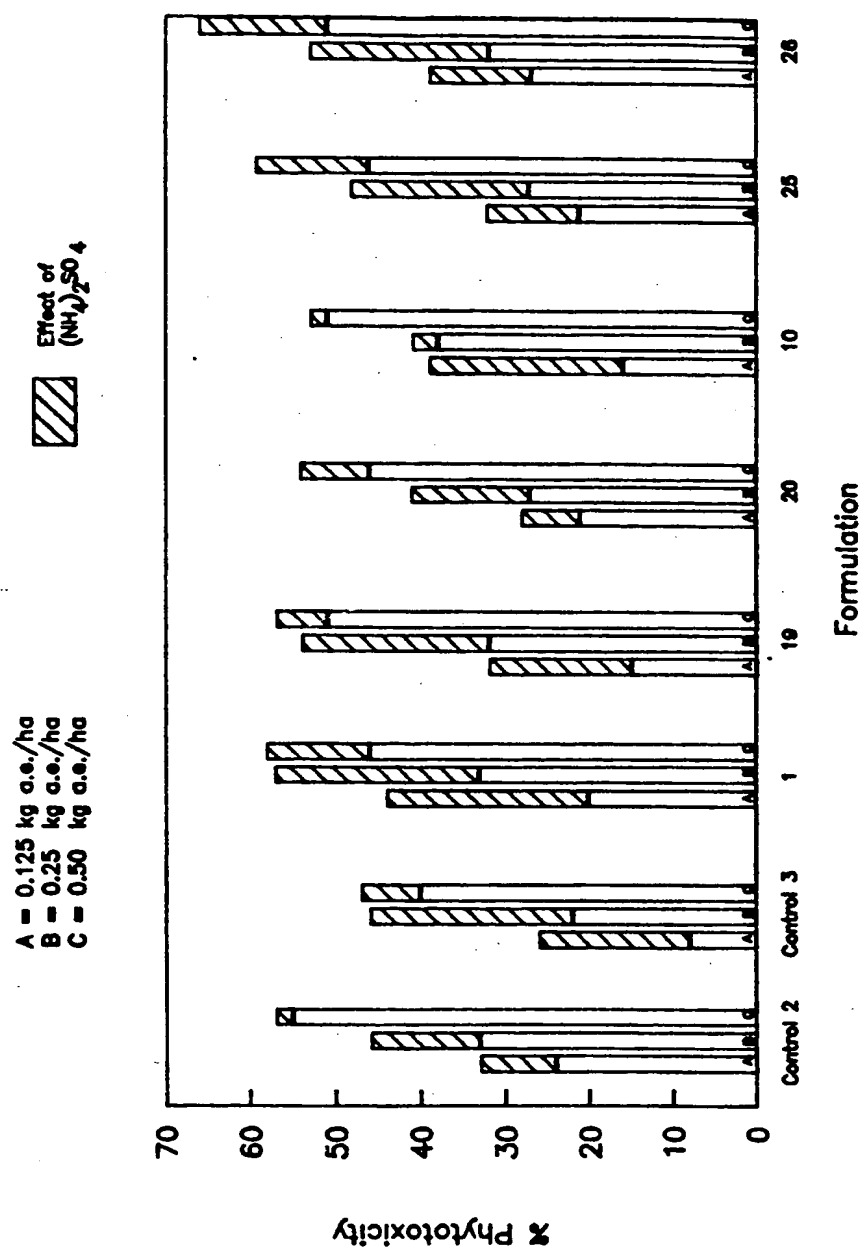


Fig. 5

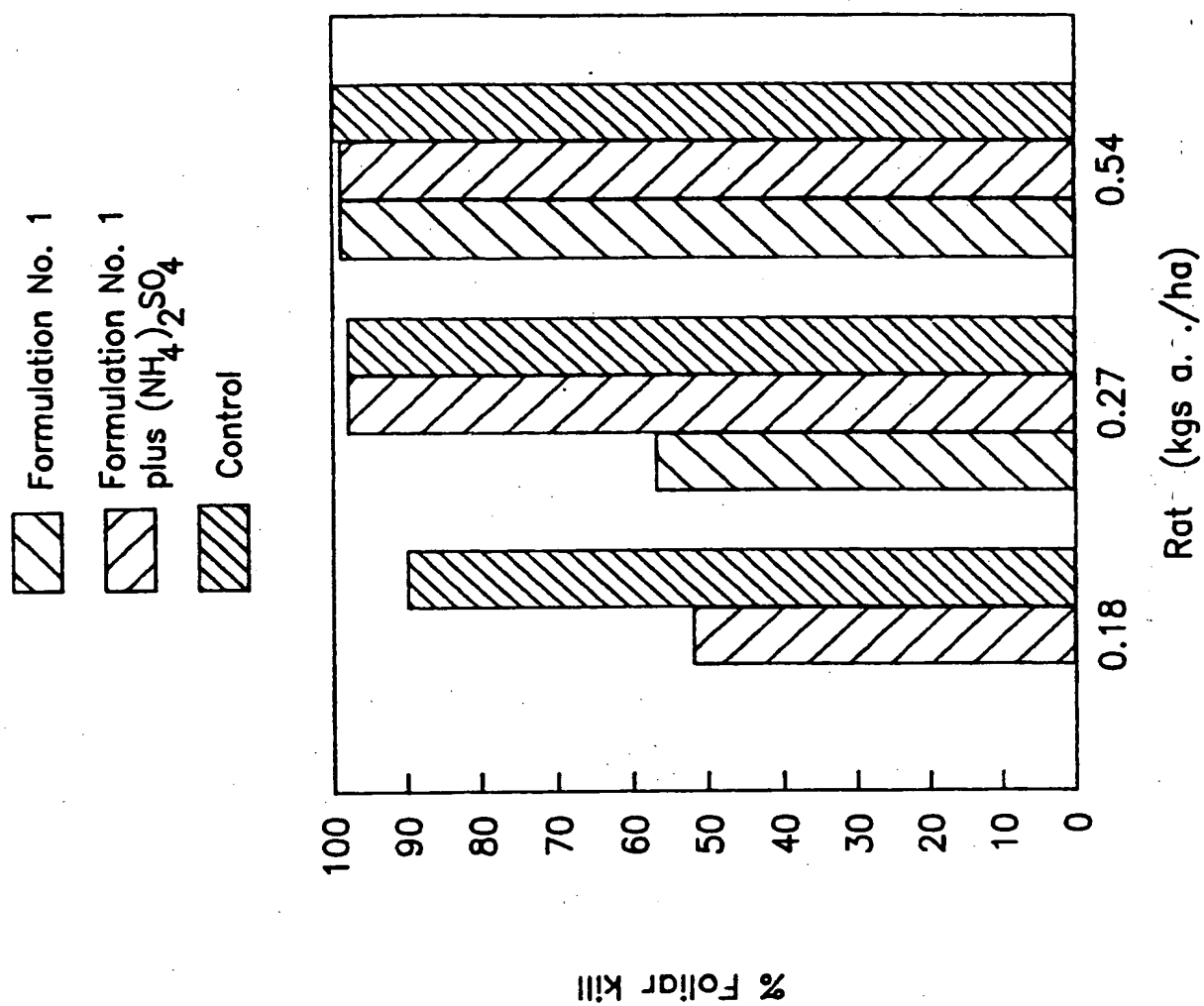


Fig.6

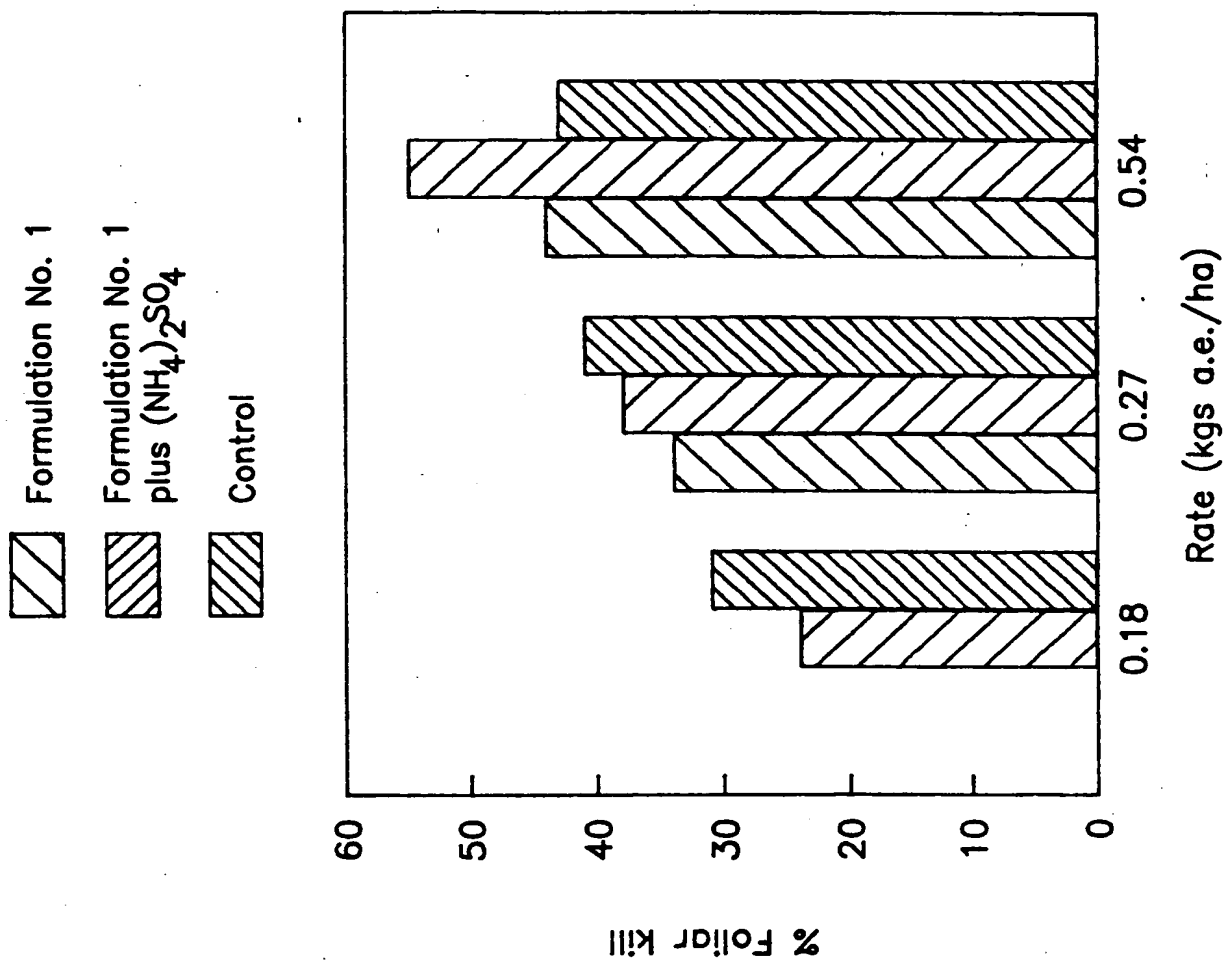




Fig. 7: Perennial Ryegrass

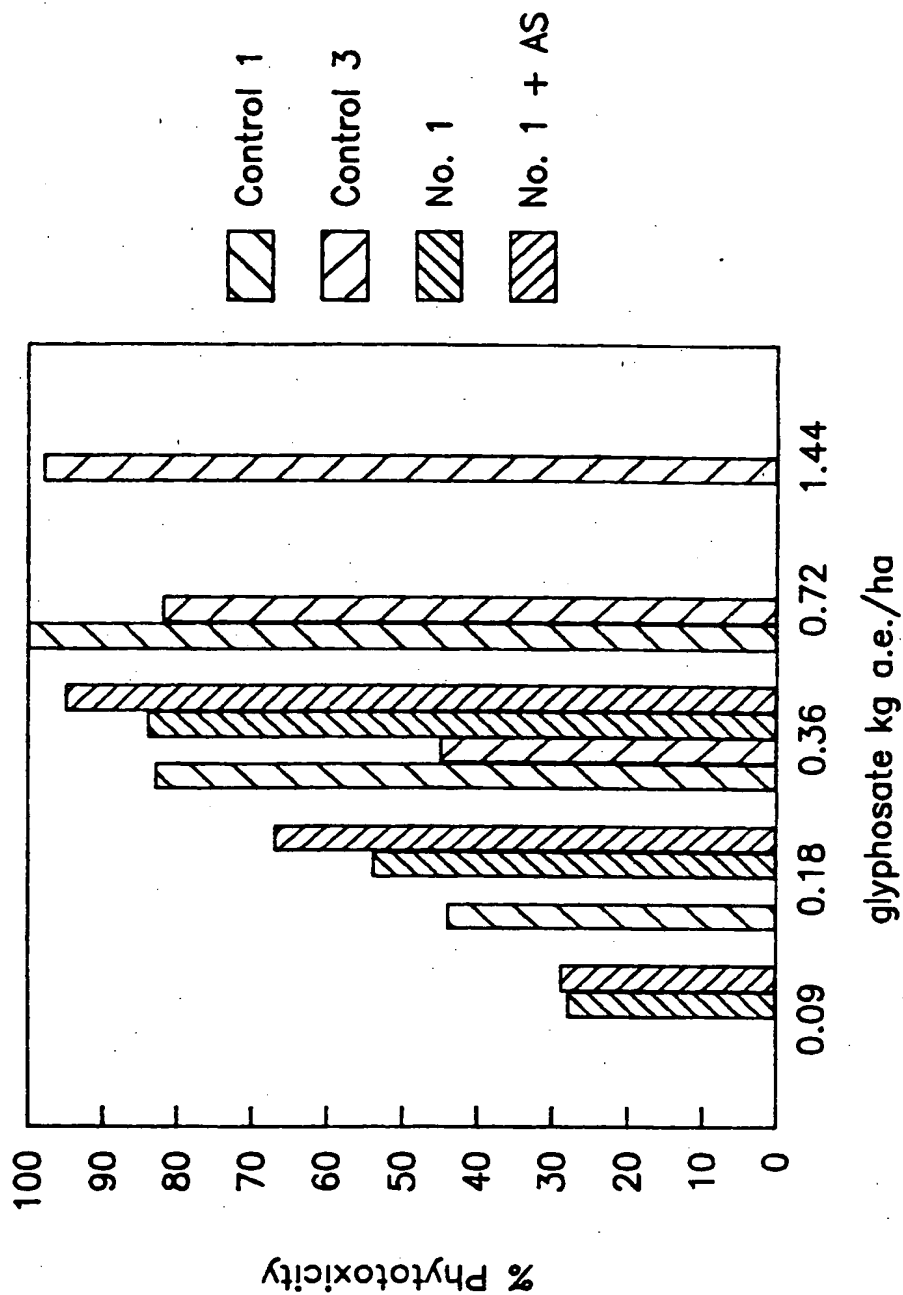


Fig 8: White Clover

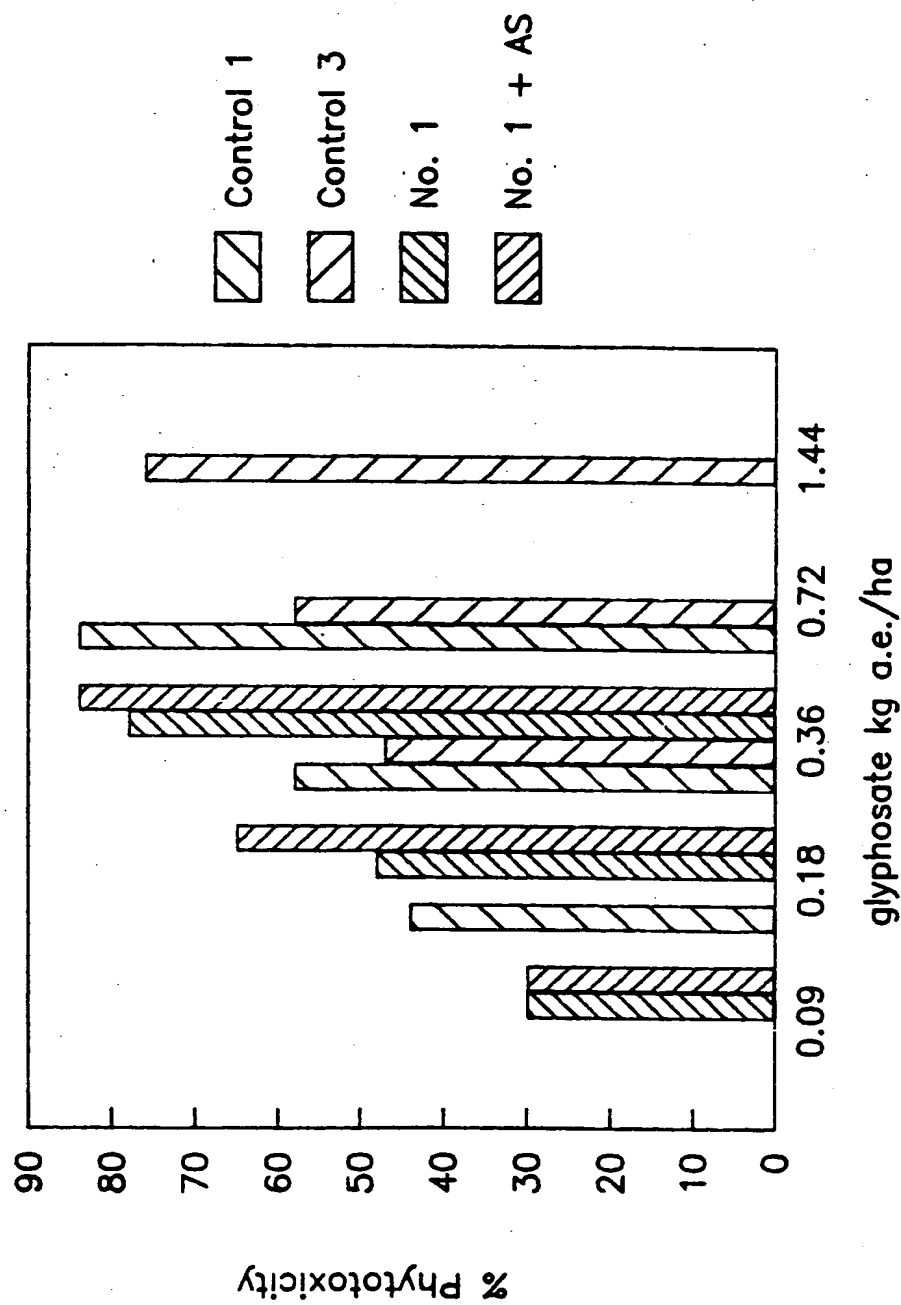


Fig 9

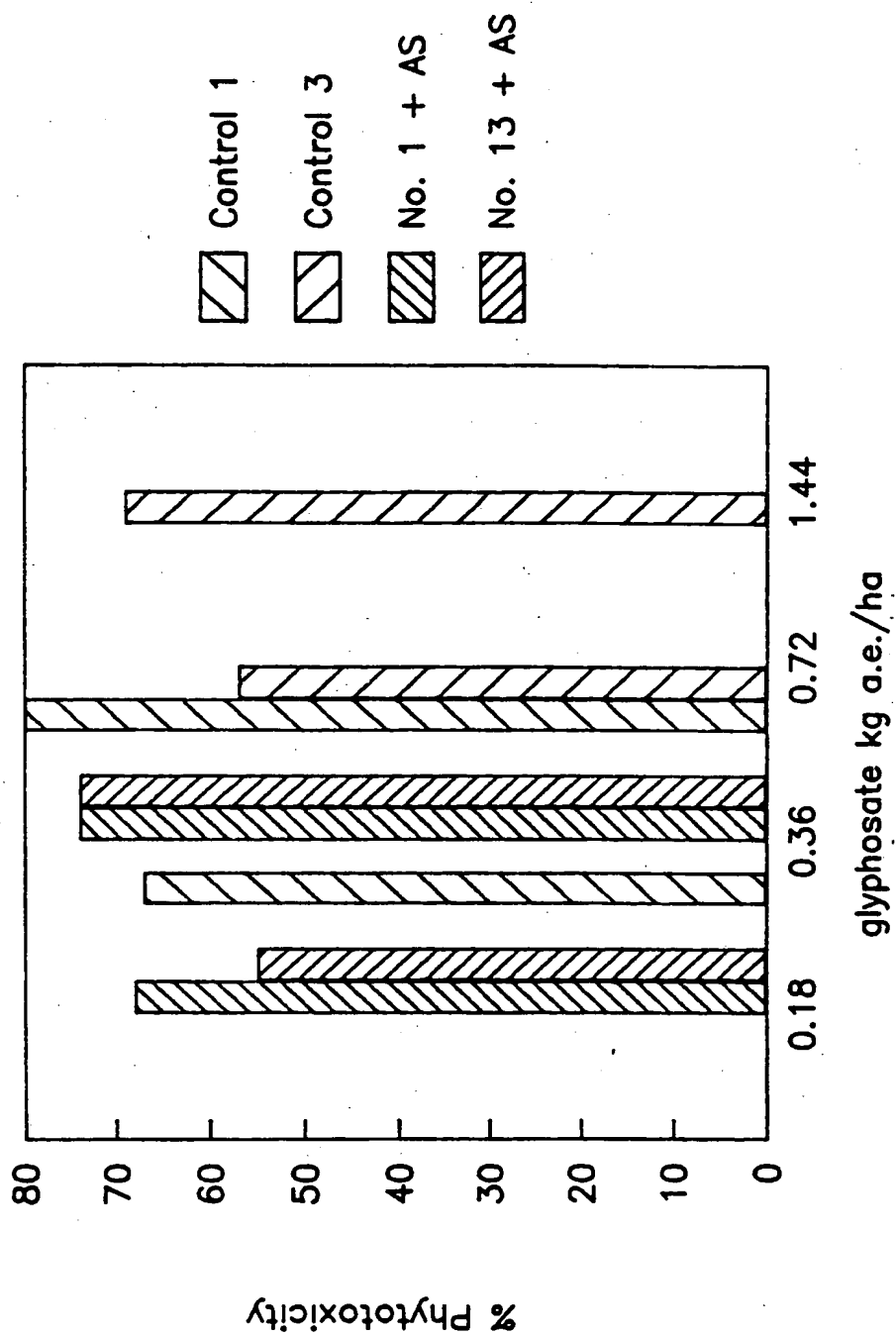


Fig 10

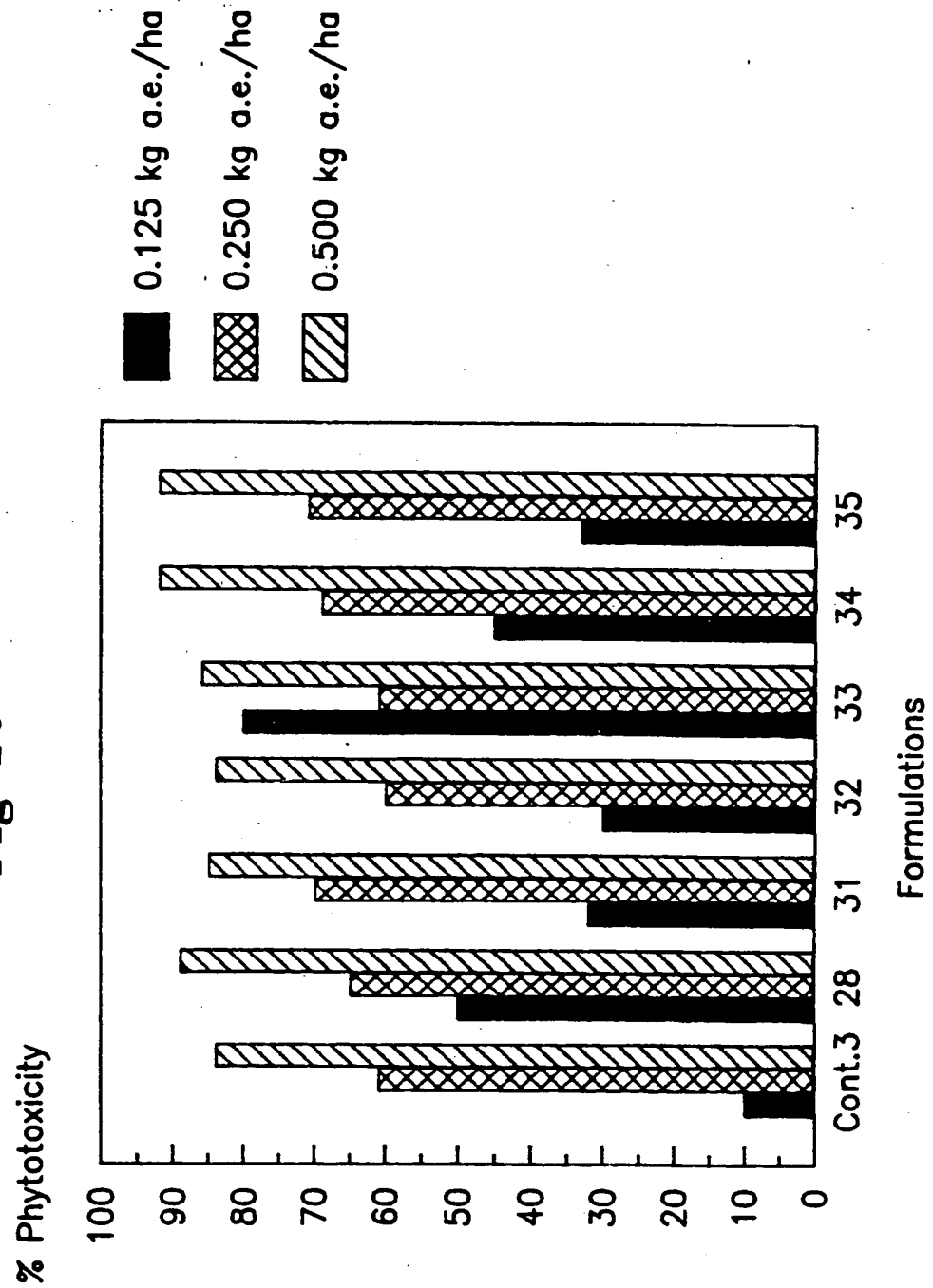
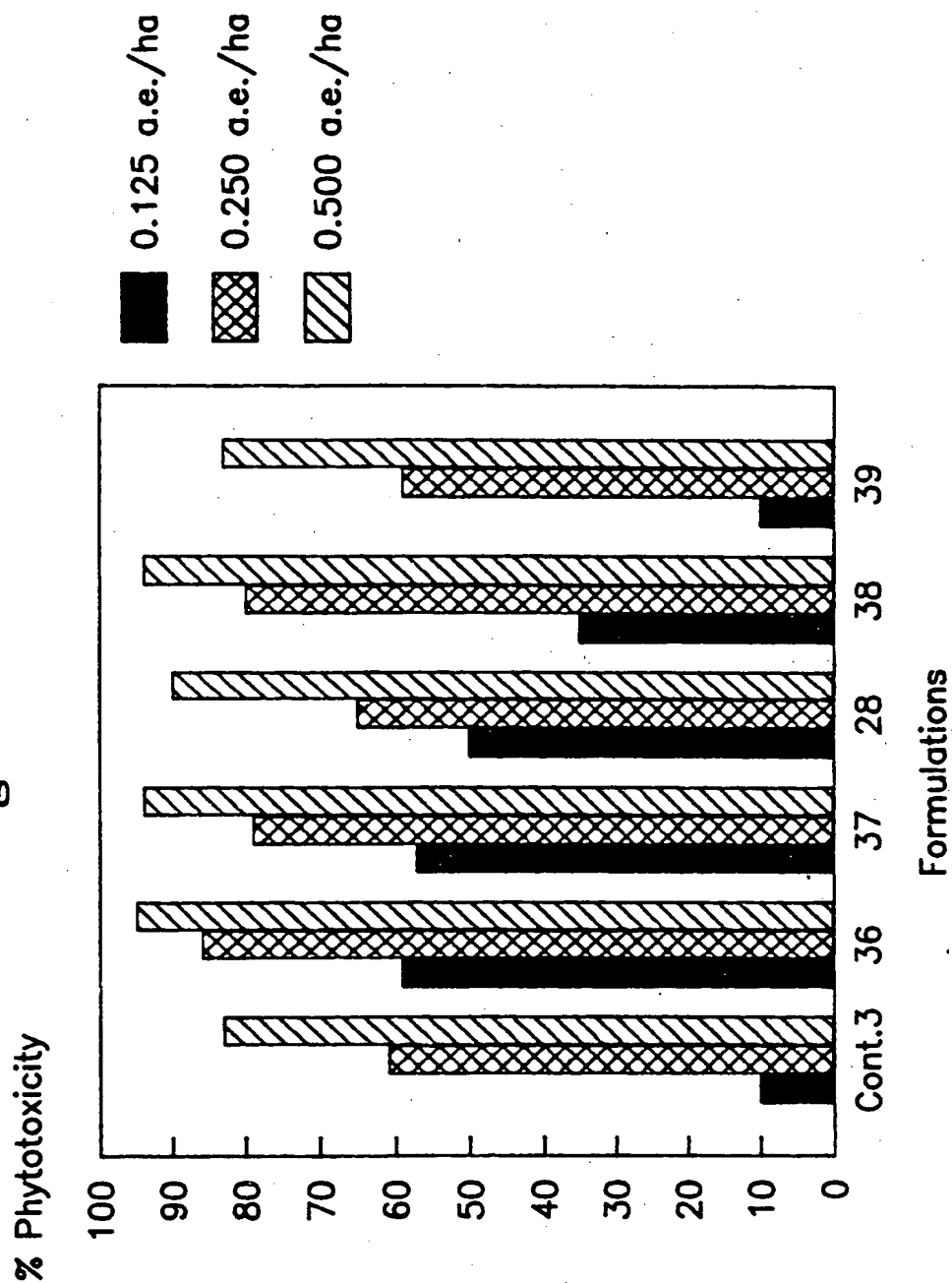


Fig 11





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Office européen des brevets

(11) Publication number:

**0 290 416**  
**A3**

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 88870068.9

(51) Int. Cl.<sup>5</sup>: A01N 25/30 , A01N 25/02

(22) Date of filing: 26.04.88

(30) Priority: 29.04.87 GB 8710164  
04.09.87 GB 8720819

(43) Date of publication of application:  
09.11.88 Bulletin 88/45

(84) Designated Contracting States:  
AT BE CH DE ES FR GB GR IT LI LU NL SE

(68) Date of deferred publication of the search report:  
21.03.90 Bulletin 90/12

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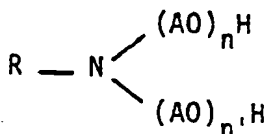
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(54) Improved glyphosate formulations.

(57) Concentrates containing glyphosate herbicide which on dilution give spray solutions having higher herbicidal unit activity than prior art solutions comprise:

(a) solubilised glyphosate equivalent to at least 40 grams per litre of glyphosate acid; and

(b) a surfactant which is (i) an amine having the formula



where R represents a straight- or branched-chain alkyl or alkenyl group having from about 8 to about 22 carbon atoms, A represents an alkylene group,

for example an ethylene or propylene group, and n and n' are integers such that n + n' has a value of from 1 to about 12, (ii) a mixture of such amines having different groups R, the average number of carbon atoms in the groups R being from about 8 to about 22, or (iii) a mixture of such amines having different values of n and n', n and n' being integers such that in individual amines n + n' can have a value from 0 to about 15, but in the mixture the average of the sum of n + n' is from 1 to about 12, R having a single value or an average value as in a mixture (ii); and wherein the weight ratio of (a) (expressed as glyphosate acid equivalent) to (b) is from about 1:1.75 to about 6:1.

EP 0 290 416 A3



EP 88 87 0068

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	CHEMICAL ABSTRACTS, vol. 102, no. 15, 15th April 1985, page 215, abstract no. 127180p, Columbus, Ohio, US; L.S. MORROW: "Effect of rate of glyphosphate with and without frigate surfactant on weed control in orbit spring oats", & PROC. ANNU. MEET. NORTHEAST. WEED SCI. SOC. 1985, 39, 112-13 * Abstract * ---	1-12, 19	A 01 N 25/30 A 01 N 25/02
X	US-A-4 528 023 (J.L. AHLE) * Whole document * ---	1-4, 11, 19	
L	CHEMICAL ABSTRACTS, vol. 110, no. 15, 10th April 1989, page 271, abstract no. 130514w, Columbus, Ohio, US; & PL-A-131 437 (INSTYTUT PRZEMYSŁU ORGANICZNEGO), (Cat. X) 30-10-1986 (Polish patent published 30-10-1986 chem. abs. gives abstract of contents and details of patent publication) ---	1-7	
D, A	WEED RESEARCH, vol. 20, 1980, pages 139-146, European Weed Research Society, Oxford, GB; D.J. TURNER et al.: "Effect of ammonium sulphate and other additives upon the phytotoxicity of glyphosate to Agropyron repens (L.) Beauv" * Page 140, table 1; page 142, table 6; page 143, tables 7, 9; page 144, discussion * --- -/-	1-25	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) A 01 N
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01-12-1989	Examiner FLETCHER A. S.
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
D,A	1985 BRITISH CROP PROTECTION COUNCIL MONOGRAM NO. 28, SYMPOSIUM ON APPLICATION AND BIOLOGY, 1985, pages 135-144; D.J. TURNER et al.: "Studies with alternative glyphosate formulations" * Page 137, table 1; page 138, lines 20-50; page 141, tables 5,6; page 142, table 7; page 143, tables 8,9; page 144, discussion * -----	1-25	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
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Place of search THE HAGUE		Date of completion of the search 01-12-1989	Examiner FLETCHER A.S.
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